Crystal structure and magnetic ordering of Pr in $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$

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The crystal structure of polycrystalline $PbBaSrPrCu_3O_8$ was studied using high resolution neutron diffraction. Rietveld refinement of the diffraction pattern shows that the compound crystallizes into the $Tl_2Ba_2YCu_2O_8$ 2212-type structure. The Pb and Cu atoms in the two (Pb,Cu)O layers are randomly mixed to form two $(Pb_{0.5}Cu_{0.5})O$ layers, and the Ba and Sr atoms are also randomly mixed to form two $(Ba_{0.5}Sr_{0.5})O$ layers, resulting in $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$. The magnetic ordering of the Pr ions was also studied using magnetic neutron diffraction and ac susceptibility measurements. At low temperatures, magnetic peaks presumably originating from the Pr spin ordering were observed at the {1/2 1/2 1/2 1/2}, {1/2 1/2 3/2}, and {1/2 1/2 5/2} positions. The Pr spins order at $T_N \approx 9$ K with the moment direction along the c axis and the nearest-neighbor spins coupled antiferromagnetically. A cusp associated with the antiferromagnetic ordering at T_N is also clearly observed in ac susceptibility measurements. © *1997 American Institute of Physics.* [S0021-8979(97)33308-8]

Since the discovery of the $RBa_2Cu_3O_{6+x}$ (R=rare earth) compounds, it was soon realized there are three types of magnetic sites in the systems: one associated with the rare earth and the other two with the Cu. Most of the rare earths order at very low temperatures (~1 K), except for Pr which orders at a much higher temperature. For $PrBa_2Cu_3O_7$ both specific heat and susceptibility show anomalies at $T=17$ K,[1,2] and neutron diffraction experiments established that the transition is magnetic. All the evidence strongly suggested that the origin of this transition is Pr spin ordering,[3] and this argument has been generally accepted. However, this is in contrast to a recent NMR study[4] that concluded there is essentially no magnetic moment on the Pr ions. In this articles, we report neutron diffraction and ac susceptibility studies made on the Pr ordering in $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$, where no CuO chains are present.

About 10 g of the polycrystalline sample were prepared by the standard solid-state reaction techniques from fine powders. The details of the preparation procedure can be found elsewhere.[5] The crystal structure of the compound obtained was studied using neutron diffraction measurements. Diffraction patterns covering a range of scattering angles $5° \leqslant 2\theta \leqslant 120°$ were taken with $\lambda=1.5454$ Å neutrons on BT−1, the 32-detector high resolution powder diffractometer at the research reactor operated by the U.S. National Institute of Standards and Technology (NIST). The angular collimations used were 14′-20′-7′ full width at half maximum (FWHM) before and after the Cu(311) monochromator and after the sample, respectively. The high resolution diffraction pattern obtained at room temperature was analyzed by the Rietveld refinement[6,7] method, using the $Tl_2Ba_2YCu_2O_8$ 2212-type structure with space group $I4/mmm$.[8] The Pb and Cu atoms in the two (Pb,Cu)O layers are assumed to be randomly mixed to form two $(Pb_{0.5}Cu_{0.5})O$ layers, rather than forming two separated PbO and CuO layers. The same situation also occurs in the two (Ba,Sr)O layers, where the Ba and Sr atoms are assumed to be evenly mixed. A good fit to the observed diffraction pattern is obtained with room temperature lattice parameters $a=b=3.8947(3)$ Å and $c=27.4925(7)$ Å.

The variation of the ac susceptibility with temperature was also measured to study the response of the system to a driving magnetic field. During the measurement, the sample was loaded into a cylindrical plastic container and a conventional ^{4}He flow cryostat was used to cool the sample. Both the in-phase component χ' and the out-of-phase component χ'' were measured over a temperature range of 4.5–320 K using various driving fields with and without an applied dc magnetic field. Figure 1 shows the temperature dependence of χ' measured using a driving field of strength 1 Oe rms and frequency 1000 Hz. Measurements made using a different strength or a different frequency for the driving field generated essentially the same results. At high temperatures $\chi'(T)$ follows Curie–Weiss behavior. The solid curve shown in Fig. 1 is a fit of the data to $\chi_0' + C/(T+\theta)$, where χ_0' is a constant. The effective moment μ_{eff} that we obtained using the fitted value for the Curie–Weiss constant C is 2.95(5) μ_B. This value for μ_{eff} lies between 3.58 μ_B for free Pr^{3+} ions and 2.54 μ_B for free Pr^{4+} ions, indicating a mixed valence character for the Pr ions.

$\chi'(T)$ is seen to depart from the Curie–Weiss curve as the temperature approaches 10.5 K, as shown in the inset in Fig. 1. At this temperature a measurable value of χ'' also develops. At even lower temperatures, a cusp in $\chi'(T)$ and a peak in $\chi''(T)$ are clearly revealed, as shown in Fig. 2. The behavior observed for $\chi'(T)$ and $\chi''(T)$ signifies the antiferromagnetic ordering of the Pr spins. The effects of a dc field on the cusp in $\chi'(T)$ and the peak in $\chi''(T)$ are also shown in

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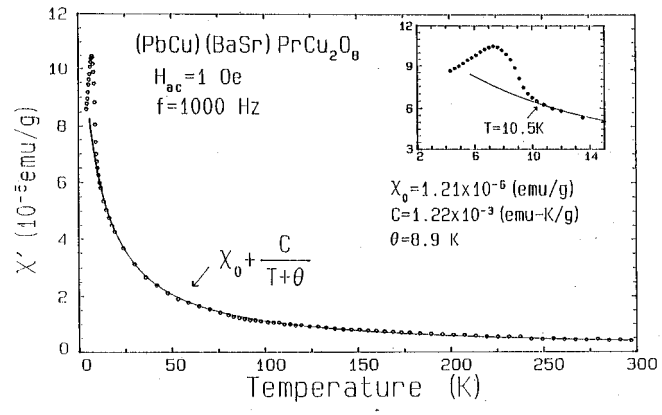

FIG. 1. Temperature dependence of the in-phase component of the ac susceptibility. The solid curve is the fit of the high temperature data to the Curie–Weiss law. A cusp which signifies the Pr spin ordering is evident at low temperatures.

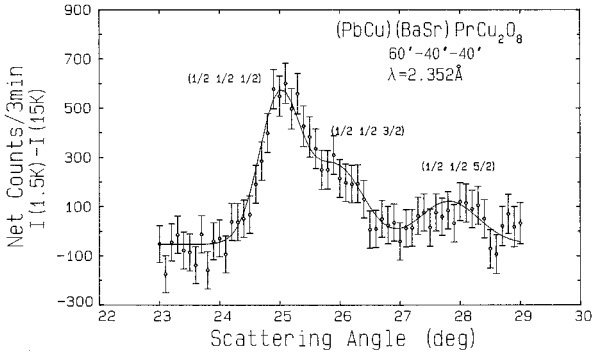

FIG. 3. Magnetic diffraction pattern observed at $T=1.5$ K. Three magnetic peaks are evident, and may be indexed as the {1/2 1/2 1/2}, {1/2 1/2 3/2}, and {1/2 1/2 5/2} reflections.

Fig. 2. Clearly, both the cusp in $\chi'(T)$ and the peak in $\chi''(T)$ are strongly affected by the applied dc field. Above 12 K no obvious changes of χ' and χ'' were found as a dc field with strength up to 10 kOe was applied. These results show that 10 kOe is not strong enough to significantly alter the paramagnetic Pr spins. At low temperatures, on the other hand, both the cusp in $\chi'(T)$ and the peak in $\chi''(T)$ shift downward and their maxima move to higher temperatures as a dc field was applied. These behaviors indicating the Pr spin ordering may have been weakened or destroyed by the applied dc field. The couplings between the Pr spins are hence mainly antiferromagnetic in nature.

Neutron diffraction measured at low temperatures was also carried out to study the Pr spin ordering. The magnetic diffraction patterns were collected on the NIST BT-2 triple-axis spectrometer operated in double-axis mode, with 2.44 Å neutrons defined by a pyrolytic graphite PG(002) monochromator. A PG filter was used to suppress higher-order wavelength contaminations, and angular collimations employed were $60'-40'-40'$ FWHM acceptance. A pumped ^{4}He cryostat was used to cool the sample. Two sets of diffraction patterns taken at 1.5 and 15 K were collected, covering a range in scattering angle from 7° to 42°. At $T=1.5$ K, besides the nuclear Bragg peaks, there are also Bragg peaks presented at the $\{1/2\ 1/2\ l\}$ positions, with l=half integers as indexed on the nuclear unit cell. Figure 3 shows a portion of the difference between the diffraction patterns taken at $T=1.5$ and $T=15$ K. This plot gives the peaks that develop as the temperature is reduced from 15 to 1.5 K. The solid curves shown in Fig. 3 are the fits of the data to the Gaussian resolution function. Three magnetic peaks indexed as the {1/2 1/2 1/2}, {1/2 1/2 3/2}, and {1/2 1/2 5/2} reflections are observed, which we believe originate from the ordering of the Pr spins. The magnetic unit cell hence doubles the nuclear one along all three crystallographic directions. The moment direction, as determined from the intensity ratios between the observed magnetic peaks, is along the c-axis direction. By comparing the {1/2 1/2 1/2} magnetic intensity observed at $T=1.5$ K with the {002} nuclear intensity, we obtain $\langle\mu_z\rangle=0.56(5)\ \mu_B$ for the saturated moment on each Pr ion. This observed moment is somehow smaller than the Pr moment found in other high-T_c oxides. We believe that the difference in the saturated moment found for Pr in difference high-T_c compounds is likely due to their different levels of hybridization as well as the difference in their crystalline electric field environment.

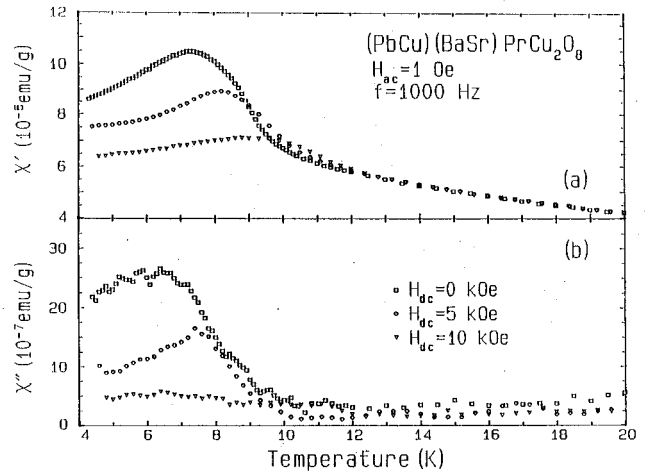

FIG. 2. Effect of an applied dc field on the cusp in the in-phase component and the peak in the out-of-phase component of the ac susceptibility observed at low temperatures.

The variation of the {1/2 1/2 1/2} peak intensity with temperature is shown in Fig. 4, which reveals a typical order parameter for powder samples.[9] Within experimental accuracy no hysteresis was observed. On cooling, the intensity starts to grow around 10 K, increasing in the usual way and reaching saturation around 4 K. The ordering temperature for the Pr spins is then determined to be at $T_N\approx 9$ K. This ordering temperature matches the temperature at which $d\chi'/dT$ shows a minimum. The inset in Fig. 4 shows the proposed Pr spin structure with which the nearest-neighbor Pr spins in the tetragonal ab plane are aligned antiparallel, and the net interlayer interactions between the nearest-neighbor layers are zero due to the exact cancellation.

In conclusion, neutron diffraction and ac susceptibility

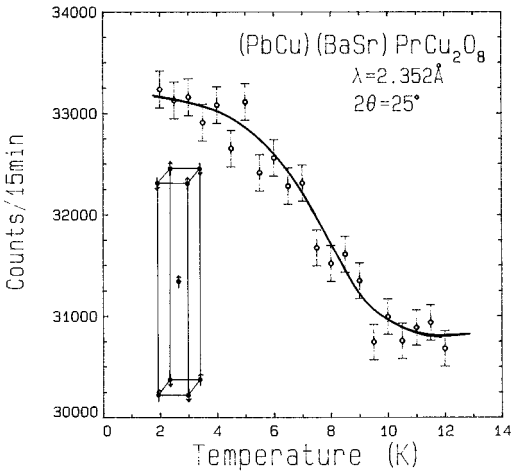

FIG. 4. Variation of the {1/2 1/2 1/2} peak intensity with temperature. The ordering temperature for the Pr spins is estimated to be $T_N \approx 9$ K. The solid curve shown is a guide to the eye only.

measurements were performed on polycrystalline $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$. A cusp in $\chi'(T)$ and a peak in $\chi''(T)$ were observed around $T=9$ K, which we believe is originated from Pr spin ordering. Neutron diffraction shows that the Pr spins order in a simple antiferromagnetic arrangement. This is a compound in which no CuO chains are present, and a transition around 9 K was still observed. We finally remark that $Tl_2Ba_2PrCu_2O_8$ is another compound in which no CuO chains are present but a transition at $T=8$ K that presumably is originated from Pr spin ordering has also been observed.[10]

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[1] C.-S. Jee, A. Kebede, D. Nichols, J. E. Crow, T. Mihalisin, G. H. Myer, I. Perez, R. E. Salomon, and P. Schlottmann, Solid State Commun. **69**, 379 (1989).
[2] For a review, see H. B. Radousky, J. Mater. Res. **7**, 1917 (1992); J. W. Lynn, J. Alloys Compd. (in press).
[3] W-H. Li, J. W. Lynn, S. Skanthakumar, T. W. Clinton, A. Kebede, C.-S. Jee, J. E. Crow, and T. Mihalisin, Phys. Rev. B **40**, 5300 (1989).
[4] K. Nehrke and M. W. Pieper, Phys. Rev. Lett. **76**, 1936 (1996).
[5] C. L. Yang, J. H. Shieh, Y. Y. Hsu, H. C. Ku, and J. C. Ho, Phys. Rev. B **52**, 10452 (1995).
[6] H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).
[7] *The Rietveld Method*, edited by R. A. Young (Oxford University Press, New York, 1993).
[8] H. Shaked, P. M. Keane, J. C. Rodriguez, F. F. Owen, R. L. Hitterman, and J. D. Jorgensen, *Crystal Structure of the High-T_c Superconducting Copper-Oxides* (Elsevier Science, British Vancouver, 1994).
[9] G. E. Bacon, *Neutron Diffraction*, 3rd ed. (Oxford University Press, Oxford, 1975).
[10] W. T. Hsieh, K. J. Chang, W.-H. Li, K. C. Lee, J. W. Lynn, C. C. Lai, and H. C. Ku, Phys. Rev. B **49**, 12200 (1994).